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(54) Title: BASE OIL FOR WELL-BORE FLUIDS

(57) Abstract

A base oil for well-bore fluids, such as drilling fluids, comprising normal alkanes having from 11 to 16 carbon atoms, with no more than a trace of the normal alkanes having greater than 16 carbon atoms, and having a pour point at less than -2 °C, as well as low toxicity and good aerobic and anaerobic biodegradability.

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BASE OIL FOR WELL-BORE FLUIDS

The present invention relates to base oils for use in well-bore fluids, such as drilling fluids, to well-bore fluids incorporating the base oil and to the use of such fluids.

Well-bore fluids, for example drilling fluids, are used in oil and gas recovery and in geothermal energy and mineral exploration and extraction operations. The fluid serves a number a functions including removal of drilled cuttings from the bore-hole and sealing of the well-bore surfaces so that fluid loss into the formation being drilled is minimised. The fluid also lubricates and cools the drill pipe during the drilling operation.

Oil based drilling fluids have been used for around 50 years for drilling underground formations to recover oil and gas. Oil based fluids are preferred systems compared with water-based formulations, especially where highly water-sensitive underground formations are being drilled. In water-based fluids water tends to migrate from the fluid to the formation being drilled. This destabilizes the formation and can lead to disintegration and breakdown of the bore-hole. Furthermore, water-based fluids tend to be unsuitable for use at high temperatures and where highly deviated bore-holes may be required to reach the targeted formations.

In view of the disadvantages of water-based fluids the recent trend has been to use drilling fluids which are oil-based. However, oil-based fluids previously used containing base oils such as diesel and crude oil, are toxic and only slightly biodegradable. This is obviously unsatisfactory with respect to environmental health and safety considerations, especially as drill cuttings coated with or containing the fluid are usually discharged to the sea floor when drilling off-shore. The use of these kinds of oil-based fluids can have a detrimental effect on marine organisms.

It has been proposed to use mineral oils as the base oil in drilling fluids instead of other petroleum derived oils. However, while less toxic than these other petroleum based drilling fluids mineral oil based fluids are not very biodegradable. Surveys on drill cuttings on the seabed of the North Sea have confirmed the persistence of mineral oils.

More recently attention has focused on the use of esters, ethers and white oils as base oils. These have improved toxicity characteristics, approaching that of water, and have reasonably good aerobic biodegradability. However, with the exception of the esters they typically exhibit poor anaerobic biodegradation. Anaerobic biodegradation is required, for example, at the sea floor. Also, these base oils tend to have high kinematic viscosities and temperature limitations. Furthermore, with the exception of the white oils they are very expensive when compared to the kinds of mineral oils described above.

The present invention seeks to provide a base oil for use in oil-based well-bore fluids, such as drilling fluids, which overcomes the disadvantages discussed above. In particular, the present invention seeks to provide a base oil which has low toxicity, good aerobic and anaerobic biodegradability and a combination of physical characteristics which are especially well suited to its use as a well-bore fluid. It is also an object of the invention to provide a base oil which is inexpensive.

Accordingly, the present invention resides in the use as base oil in a well-bore fluid of a mixture comprising at least 70% by weight of one or more normal alkanes having from 11 to 16 carbon atoms, wherein the mixture has a pour point of less than -2°C.

The mixture typically comprises 30% by weight, or less, of one or more branched or cyclic alkanes having from 11 to 16 carbon atoms.

As it is extremely important that the base oil biodegrade as quickly as possible it is preferred that the mixture comprises a very high proportion of normal (straight chain) alkanes. Branched-chain and cyclic hydrocarbons are not broken down by bacteria as rapidly as normal hydrocarbons. According to a preferred embodiment of the invention the mixture comprises at least 90% by weight of the one or more normal alkanes. More preferably the mixture comprises at least about 98% by weight of the one or more normal alkanes. Mixtures of normal alkanes having from 11 to 16 carbon atoms are most preferably used.

The toxicity to flora and fauna of base oils used in drilling fluids is believed to be directly linked to aromatic content. To minimise toxicity therefore the aromatic

content in the mixture must be kept as low as possible, 0.1% by weight being the typical maximum allowed.

The pour point of drilling fluids is a particularly important characteristic as it is essential that the fluid is capable of being pumped at the lowest temperature encountered during mixing, storage, transportation and use. The pour point of the fluid is primarily influenced by the pour point of the base oil which is used.

In PCT patent application WO 95/06694, published on March 9, 1995, there is an indication on its page 4, lines 12-16, that when using normal alkanes as a drilling fluid in a cold environment, one may use a pour point depressant to reduce the pour point (freezing point) of the fluid.

In accordance with the present invention the base oil mixture has a pour point of less than -2°C, preferably -9°C or less. However, these represent the pour point of the mixture without the addition of pour point depressants. Pour point depressants could be used but they tend to be of little effect in pure normal alkane mixtures. The addition of pour point depressants may in fact lead to undesirable side-effects such as increased toxicity and low flash point. Pour point depressants may also cause decreased stability of invert emulsion well-bore fluids.

To minimise or prevent the danger of fire or explosion of oil-based drilling fluids the base oil used should have a flash point which is higher than the surface circulating temperature of the fluid during drilling of the well-bore. Preferably, the base oil used in the present invention has a flash point of at least 65°C, more preferably at least 80°C.

A further important characteristic of the base oil used is its kinematic viscosity. This is crucial to the ability of the drilling fluid to tolerate solids and water, whether added as integral components or accumulated during the mechanism of drilling into formations or by formation water intrusion. Generally, the lower the kinematic viscosity of the base oil used the higher the tolerance of the fluid is. Through practical experience it has been found that the base oil should preferably have a kinematic viscosity of from 1 to 10 cSt, more preferably from 1 to 6 cSt, at 40°C, and this is a feature of the base oil of the present invention. Base oils having a viscosity of about 1 cSt at 40°C are believed to be the most tolerant to solids and

water. Difficulty in pumping tends to be encountered when using base oils having a viscosity at 40°C of greater than 6 cSt.

Base oils which may be used in the present invention are commercially available, and tend to be produced through cracking, reaction and distillation processes.

The present invention also provides a well-bore fluid comprising as base oil the mixture as described above in combination with an emulsifier, oil-wetting agent, viscosifier, filtration control additive, rheology modifier, thinner and/or weighting agent. These are additives conventionally used in well-bore fluids and the combination which is used depends upon the desired characteristics of the fluid being formulated.

Emulsifiers which may be used include fatty acids, soaps of fatty acids and fatty acid derivatives and amidoamines, polyamides, polyamines, esters such as sorbitan monoleate polyethoxylate and sorbitan dioleate polyethoxylate, imidaxolines and alcohols.

Typical oil wetting agents which may be used include lecithin, fatty acids, crude tall oil, oxidized crude tall oil, organic phosphate esters, imidazolines, amidoamines, alkyl aromatic sulphates, alkyl aromatic sulphonates, and organic esters of polyhydric alcohols.

Typical viscosifiers include organophilic clays (eg. hectorite, bentonite and attapulgite), oil soluble polymers and resins, and polymers such as sulphonated ethylene propylene diene (EPDM) terpolymers and sulphonated butadiene styrene copolymers.

As filtration control additives which may be used there may be mentioned asphalt and derivatives thereof, gilsonite, amine-treated lignite and polymers such as EPDM terpolymers, styrene butadiene copolymers and acrylate styrene copolymers.

Typical rheology modifiers include fatty acids and polymeric fatty acids.

Thinners which may be used include petroleum sulphonates, amidoamines, alkaryl sulphonates and polyamines.

Examples of weighting agents include barite, iron oxide, iron carbonate, calcium carbonate and galena.

It is possible to use the base oils alone, i.e. without the use of the conventional additives described. Typically, however additives are required to tailor the properties of the fluid to meet specific requirements.

The well-bore fluid may be an all oil-based fluid or an invert emulsion (i.e. a water-in-oil emulsion) formed using water, brine or a polar organic liquid which is insoluble in the base oil. Preferably, the polar organic liquid is glycerol, methanol or propylene carbonate. When the well-bore fluid is an invert emulsion, the emulsified phase typically represents from 1 to 70% by volume of the fluid.

The use of fluid which is an invert emulsion enables the overall cost to be reduced by reducing the volume of base oil needed. The water activity of the invert emulsion can be adjusted by the addition of inorganic salts to balance the water activity of the formulation being drilled into. Examples of inorganic salts which may be used include the sodium, potassium, calcium, magnesium, caesium and zinc chlorides, sodium, calcium and zinc bromides, sodium, potassium and caesium formates, sodium and potassium acetates and calcium and ammonium nitrates.

The typical proportions of these additives in the well-bore fluids of the present invention are shown in the following table.

	Typical	More Typical
Base oil, Volume %	20-100	50-90
Emulsifier, lb/bbl	1-20	4-16
Oil wetting agent, lb/bbl	0-10	0.5-4
Viscosifier, lb/bbl	0-15	1-6
Filtration control additive, lb/bbl	0.5-25	1-10
Rheology modifier, lb/bbl	0-4	0.5-2
Thinner, lb/bbl	0-10	0.5-4
Weighting agent, lb/bbl	0-700	0-500
Water, Volume %	0-60	20-50
Calcium Chloride, lb/bbl (to adjust water activity)	0-150	2-100

In this table lb/bbl represents pounds per US barrel. The well-bore fluids of the present invention are prepared by conventional techniques by mixing of the

constituents. Preparation of the oil-based drilling fluid may take place at a land-based mud-mixing facility, or at the well-site. Mixing typically takes place in tanks equipped with circulating centrifugal pumps and agitation/shear equipment.

Although primarily described as a drilling fluid, the base oil described is suitable for use generally as a well-bore fluid. The base oil can be used for example as a pay zone drill in fluid, a completion fluid, a "kill" fluid, a packer fluid or casing pack, a "spotting" fluid or a "spacer".

The invention further provides a method of drilling using a well-bore fluid of the invention as described above.

The following Examples illustrate the present invention. Unless otherwise states US gallons and barrels are referred to herein.

Example 1

A laboratory barrel (350ml) of drilling fluid was prepared by mixing the various ingredients shown in the table below using a Silverson mixer at a speed of 6,000 rpm using a square hole disintegrator head. The total mixing time was 1 hour and the ingredients were added in the order listed, a period of five minutes being allowed between each ingredient addition. A water bath was used to maintain the temperature below 65°C (150°F).

TABLE 1

Ingredient	Amount	Function
Base oil A	136 ml	Base oil
EZ MUL 2F[1]	10 g	Emulsifier
GELTONE II[1]	2.5 g	Viscosifier
Lime	4 g	Alkalinity Control
DURATONE HT[1]	4 g	Filtration Control
Freshwater	136 ml	Emulsified Phase
Barite	163 g	Weighting Agent
Calcium Chloride (82% pure)	60 g	Water Activity Balance
RM-63[1]	1 g	Rheology Modifier

[1] - available from Baroid Limited

The fluid formed has the following properties:

Density	:	1.38kg/m^3 (11.5lb/gal)
Oil/Water Ratio	:	50/50
Water Phase Salinity	:	250,000 ppm calcium chloride

Base oil A has the following composition and properties:

	wt %
n-C_{11}	9.1
n-C_{12}	21.7
n-C_{13}	36.2
n-C_{14}	31.3
n-C_{15}	1.4
n-C_{16}	0.04
$>C_{16}$	trace
aromatics	<0.1

Pour point	= -9°C
Flash point	= 91°C
Kinematic Viscosity at 40°C	= 1.75cSt

The properties of base oil A compared with some commercially available North Sea base oils is illustrated in Table 2 below.

TABLE 2

Base Oil	Density g/ml @ 15°C	Flash Point °C (PMCC)	Aromatics % (Max)	Aniline Point °C	Kin. Viscosity cst at 40°C	Pour Point °C
Test Procedure	ASTM D129	ASTM D93	ASTM D2887	ASTM D611	ASTM D445	ASTM D97
Base Oil A	0.759	91	0.1	93	1.75	-9
BP 83 HF	0.790	95	4.5	88	2.40	-10
Fina DMF 120	0.820	74	2.3	73	1.72	nd
Fina DMF HF	0.820	103	3.9	82	2.90	-18
Total DF1	0.800	77	0.5	77	1.73	-39
Total HDF	0.814	100	6.0	86	3.20	-30
Shellsol D90	0.805	95	0.1	78	2.00	-20
Shellsol D70	0.792	72	0.5	78	1.62	-30
Clairsol 350	0.798	78	4.1	76	1.89	-35
Clairsol 450	0.815	93	4.4	88	3.40	-20
Clairsol 350MHF	0.783	94	2.0	78	2.20	-20
PETROFREE	0.860	179	0.0	na	6.00	-30

nd - not determined
na - not applicable

It can be seen from this table that base oil A compares very favourably with the other oils which are used to formulate well-bore fluids with respect to the combination of characteristics it possesses.

Example 2

The properties of a laboratory barrel (350ml) of the fluid of Example 1 were measured in accordance with API RP 13B-2. The properties of the fluid were also measured when contaminated with 35g Hymod clay, 10% by volume seawater and 10% by volume carnalite brine. The results are shown in Table 3 below.

TABLE 3

MEASURED PROPERTIES						
		Fluid of invention		Fluid + Hymod Clay	Fluid + Seawater	Fluid + Carnalite Brine
Hot Rolled (250°F)	hours	-	16	16	16	16
Fann 35 Readings at 120°F:						
600	rpm	85	101	159	118	96
300	rpm	55	61	104	72	59
200	rpm	43	45	85	54	45
100	rpm	33	30	61	35	30
6	rpm	16	13	26	14	11
3	rpm	14	12	24	13	10
Plastic Viscosity,	cp	28	40	55	46	37
Yield Point,	$lb/100ft^2$	27	21	49	26	22
10 sec Gel,	$lb/100ft^2$	14	13	30	13	9
10 min Gel,	$lb/100ft^2$	20	20	40	20	10
Electrical Stability	V	288	345	209	122	130
HPHT Filtrate, at 250°F,	ml	-	2.8	3.0	3.6	3.2

This table shows that the well-bore fluid of the invention is very stable to contaminants. It should be noted that the well-bore fluid exhibits very good, low rheological properties even though the water content of the fluid is 50% by volume. This shows how the low kinematic viscosity of the n-alkane mixture base oil contributes to the ability of the fluid to tolerate high added concentrations of water, and water as a contaminant.

Example 3

Following the same procedure as Example 1 a laboratory barrel (350ml) of well-bore fluid was prepared. The ingredients were mixed in the order listed in Table 4 below. Base oil A was the same as that used in Example 1.

TABLE 4

Ingredient	Amount	Function
Base Oil A	147 ml	Base oil
EZ MUL 2F[1]	20 g	Emulsifier
DURATONE HT[1]	11 g	Filtration Control
XP-10[1] (Experimental product)	3.5 g	Filtration Control
BENTONE 38[2]	0.5 g	Viscosifier
SUSPENTONE[1]	4 g	Viscosifer
Lime	4 g	Alkalinity Control
Freshwater	28 ml	Emulsified Phase
Barite	589 g	Weighting Agent
Calcium Chloride (82% pure)	9.7 g	Water Activity Balance
RM-63[1]	0.75 g	Rheology Modifier

[1] - available from Bariod Limited
[2] - available from Rheox

The fluid formed has the following properties:

Density	: 2.24kg/m^3 (18.67 lb/gal)
Oil/Water Ratio	: 85/15
Water Phase Salinity	: 250,000 mg/L calcium chloride

<u>EXAMPLE 4</u>

Example 2 was repeated using a laboratory barrel of the well-bore fluid of Example 3. The contaminants used were Hymod clay (35g) and seawater (10% by volume). The fluid was hot rolled at the temperatures shown in Table 5 below. This table shows the properties of the fluid.

TABLE 5

MEASURED PROPERTIES									
		Fluid of the Invention				Fluid + Hymod Clay		Fluid + Seawater	
Hot Rolled (350°F)	hours	-	16	-	-	-	-	-	-
Hot Rolled (395°F)	hours	-	-	16	-	16	-	16	-
Static Aged (395°F)	hours	-	-	-	16	-	16	-	16
600/300	rpm	130/75	132/78	131/74	165/98	182/111	183/120	136/85	168/109
200/100	rpm	58/38	61/40	58/37	74/48	88/62	97/68	67/27	87/61
6/3	rpm	12/10	16/14	14/12	17/15	28/27	28/24	16/14	24/20
Plastic Viscosity	cp	55	54	57	67	71	63	51	59
Yield Point	lb/100ft²	20	24	17	31	40	57	34	50
10 sec Gel	lb/100ft²	12	16	22	18	26	28	22	23
10 min Gel	lb/100ft²	21	21	24	26	32	36	25	28
Electrical Stability	V	1393	1218	1484	1002	1215	1560	713	1211
HTHP fluid loss, ml @ 395°F			5.4	5.8	11.2	8.2	14.0	6.4	12.0

The results confirm the stability of the fluids of the invention even when exposed at high temperature to contaminants.

What is claimed is:

1. A base oil for use in a well-bore fluid of a mixture comprising at least 70% by weight of one or more normal alkanes having from 11 to 16 carbon atoms, with no more than a trace of said normal alkanes having greater than 16 carbon atoms, wherein the mixture has a pour point of less than -2°C without containing a pour point depressant.

2. The base oil according to Claim 1, wherein the mixture comprises up to 0.1% by weight aromatics.

3. The base oil according to Claims 1 or 2, wherein the mixture comprises 30% by weight, or less, of one or more branched or cyclic alkanes having from 11 to 16 carbon atoms.

4. The base oil according to any one of Claims 1 to 3, wherein the mixture comprises at least 90% by weight of one or more normal alkanes.

5. The base oil according to Claim 4, wherein the mixture comprises at least about 98% by weight of one or more normal alkanes.

6. The base oil according to any one of the preceding claims, wherein the mixture has a pour point of -9°C or less.

7. The base oil according to any one of the preceding claims, wherein the mixture has a flash point of at least 65°C.

8. The base oil according to Claim 7, wherein the mixture has a flash point of at least 80°C.

9. The base oil according to any of the preceding claims, wherein the mixture has a kinematic viscosity at 40°C of from 1 to 10 cSt.

10. The base oil according to Claim 9, wherein the mixture has a kinematic viscosity at 40°C of from 1 to 6 cSt.

11. A well-bore fluid comprising as base oil a mixture as defined in any one of Claims 1 to 10 in combination with one or more of an emulsifier, oil-wetting agent, viscosifier, filtration control additive, rheology modifier thinner, weighting agent and/or other well-bore fluid additive.

12. A fluid according to Claim 11 comprising from 20% to 100% by weight of base oil mixture, based on the total weight of the fluid.

13. A fluid according to Claims 11 or 12 which is an all oil-based fluid.

14. A fluid according to Claims 11 or 12 which is an invert emulsion with water, brine or a polar organic liquid which is insoluble in the base oil mixture.

15. A fluid according to Claim 14, wherein the polar organic liquid is glycerol, methanol or propylene carbonate.

16. A method of drilling a well which comprises using as drilling fluid the drilling fluid defined in any one of Claims 11 to 15.

INTERNATIONAL SEARCH REPORT

International application No. PCT/US96/00993

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :Please See Extra Sheet.
US CL : 585/1,2; 507/100,103,110,111,116,117,118,119
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 585/1,2; 507/100,103,110,111,116,117,118,119

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

NONE

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

NONE

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO,A, 8302949; (Jachnik); 01 September 1983; see page 7, lines 3-4 and 21-34 and page 10, lines 4-10.	1-3
X --,P Y	WO, A 95 006694 (Sawdon); 09 March 1995; see page 2, lines 21-25, column 6, lines 5-18.	1-3 --- 1-3
Y	US,A 4,508,628 (Walker et al); 02 April 1985; see column 4, lines 45-59.	1-3
Y	US,A, 5,333,698 (Van Slyke); 02 August 1994; see column 2, lines 10-24.	1-3

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier document published on or after the international filing date
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"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search 18 APRIL 1996	Date of mailing of the international search report 14 MAY 1996
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. (703) 305-3230	Authorized officer Mpandra Roy fu ELIZABETH D. IRZINSKI Telephone No. (703) 308-3802

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US96/00993

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☒ Claims Nos.: 4-16
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest.

☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US96/00993

A. CLASSIFICATION OF SUBJECT MATTER:
IPC (6):

C09K 7/06